Supplementary Material

Cs$_2$CO$_3$-Mediated synthetic strategy for iprobenfos derivatives via thiophilic addition of $H$-phosphites on in situ generated thioaldehydes

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Table of Contents

1. General information S2
2. General procedure for Table 1 S8
3. General procedure for Table 2 S8
4. References S20
5. $^1$H, $^{13}$C, $^{31}$P & $^{19}$F NMR spectra of compounds 1 & 3 S21
1. General information

Reagents, substrates, and solvents were purchased from commercial suppliers and used without purification. Anhydrous toluene uses calcium hydride to remove water, dry, and distill. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 (Merck). Chromatography was performed using silica gel 60 (43-63 um) (Merck) and Aluminum oxide 90 neutral (MN). $^1$H, $^{13}$C, $^{31}$P, and $^{19}$F NMR spectra were using CDCl$_3$ on Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as an internal standard for $^1$H and $^{13}$C NMR analysis. Chemical shifts in $^1$H NMR and $^{13}$C NMR spectra are reported as follows: Chloroform-d (referenced to 7.26 ppm for $^1$H and 77.10 ppm for $^{13}$C). Coupling constants ($J$) are reported in hertz and peak multiplicities are reported using the following abbreviations: m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, tq = triplet of quartets, qd = quartet of doublets, br = broad signal. Low-Resolution Mass Spectrometry (LRMS) experiments were recorded on an Agilent Technologies 5977A with Agilent Technologies 7890B. High-Resolution Mass Spectrometry (HRMS) experiments were recorded on Jeol JMS-HX-110 with EI (Electron Impact) method. All the phosphites 2a & 2b commercially purchased and used without purification and all the thioaldehydes 1a-m were prepared from known literature methods.

Synthesis of trithiaporphosphinanes.

In a pre-dried 250 mL flask was added Lawesson's reagent (7 mmol, 2.8 g), Benzaldehydes (10 mmol, 1.061 g) and dry toluene (60 mL) The reaction mixture was vigorously stirred at 80 °C (oil bath) for 12 hours under nitrogen atmosphere. After completion of the reaction, the reaction mixture was filtered and solvent was removed. Then the red oil crude was purified by flash alumium oxide column chromatography (DCM/hexane = 15%) as eluent to afford the pure products 1.
2-(4-Methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane 2-sulfide (1a)

\[
\text{\begin{center}
\includegraphics{image1.png}
\end{center}}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.19 (dd, \(J = 14.6 & 9.0\) Hz, 2H), 7.50 (dd, \(J = 8.0 & 1.6\) Hz, 4H), 7.40-7.34 (m, 6H), 7.09-7.06 (m, 2H), 6.29 (d, \(J = 9.2\) Hz, 2H), 3.87 (s, 3H); \(^{13}\)C \{\(H\)\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 164.1, 137.7 (d, \(J = 8.0\) Hz), 133.8 (d, \(J = 14.0\) Hz), 129.2 (d, \(J = 14.0\) Hz), 128.0, 123.1, 122.1, 114.8 (d, \(J = 16.0\) Hz), 58.2, 55.5; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 72.8. HRMS (El) calcd for C\(_{21}\)H\(_{19}\)OPS\(_4\) [M]\(^+\) 446.0358 found: 446.0059. M.P.: 78-83 °C

2-(4-Methoxyphenyl)-4,6-di-\(m\)-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1b)

\[
\text{\begin{center}
\includegraphics{image2.png}
\end{center}}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.19 (dd, \(J = 14.7 & 8.9\) Hz, 2H), 7.32-7.23 (m, 6H), 7.15 (d, \(J = 7.0\) Hz, 2H), 7.09-7.06 (m, 2H), 6.25 (d, \(J = 9.2\) Hz, 2H), 3.88 (s, 3H), 2.34 (s, 6H); \(^{13}\)C \{\(H\)\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 164.1, 139.1, 137.6 (d, \(J = 8.0\) Hz), 133.7 (d, \(J = 13.0\) Hz), 130.1, 128.8 (d, \(J = 43.0\) Hz), 125.1, 123.2, 122.3, 114.6 (d, \(J = 16.0\) Hz), 58.3, 55.6, 21.3; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 72.7. HRMS (El) calcd for C\(_{23}\)H\(_{23}\)OPS\(_4\) [M]\(^+\) 474.0369 found: 474.0379. M.P.: 79-83 °C

2-(4-Methoxyphenyl)-4,6-di-\(o\)-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1c)

\[
\text{\begin{center}
\includegraphics{image3.png}
\end{center}}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.20-8.17 (m, 2H), 7.54-7.52 (m, 2H), 7.24-7.17 (m, 6H), 7.05-7.02 (m, 2H), 6.55 (d, \(J = 9.8\) Hz, 2H), 3.80 (s, 3H), 2.49 (s, 6H); \(^{13}\)C \{\(H\)\} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 164.0 (d, \(J = 3.4\) Hz), 136.1 (d, \(J = 8.0\) Hz), 135.2, 133.5 (d, \(J = 14.0\) Hz), 130.9, 129.1, 128.1, 126.9, 123.1, 122.2, 114.6 (d, \(J = 16.0\) Hz), 55.4 (d, \(J = 19.7\) Hz), 19.2; \(^{31}\)P NMR

2-(4-Methoxyphenyl)-4,6-di-p-tolyl-1,3,5,2-trithiaphosphinane 2-sulfide (1d)

4,6-Bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2 trithia-phosphinane 2-sulfide (1e)

2,4,6-Tris(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1f)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22-8.15 (m, 2H), 7.44-7.40 (m, 4H), 7.09-7.05 (m, 2H), 6.90-6.86 (m, 5H), 6.20 (d, $J = 8$ Hz, 2H), 3.88 (s, 3H), 3.79 (s, 6H); $^{13}$C{H} NMR (100 MHz, CDCl$_3$): $\delta$ 164.0 (d, $J = 3.0$), 160.2, 133.7 (d, $J = 13.1$ Hz), 131.9, 129.8 (d, $J = 10.0$ Hz), 129.3, 128.8, 123.2, 122.1, 114.6, 114.4, 57.8, 55.6; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 72.7. HRMS (EI) calcd for C$_{23}$H$_{23}$O$_3$PS$_4$ [M]$^+$ 506.0268 found: 506.0276.

4,6-Bis(4-fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1g)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21-8.15 (m, 2H), 7.50-7.45 (m, 4H), 7.10-7.04 (m, 6H), 6.25 (d, $J = 9.1$ Hz, 2H), 3.88 (s, 3H); $^{13}$C{H} NMR (100 MHz, CDCl$_3$): $\delta$ 164.3, 161.8, 133.7 (d, $J = 14.0$ Hz), 129.9 (d, $J = 8.2$ Hz), 122.8, 121.8, 116.3 (d, $J = 21.7$ Hz), 114.6 (d, $J = 15.9$ Hz), 57.4, 55.6; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 72.8. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -110.8. HRMS (EI) calcd for C$_{21}$H$_{17}$F$_2$OPS$_4$ [M]$^+$ 481.9868 found: 481.9871. M.P.: 130-135 °C.

4,6-Bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1i)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19-8.13 (m, 2H), 7.44-7.24 (m, 8H), 7.10-7.07 (m, 2H), 6.25 (d, $J = 9.1$ Hz, 2H), 3.88 (s, 3H); $^{13}$C{H} NMR (100 MHz, CDCl$_3$): $\delta$ 164.4, 136.0 (d, $J = 9.2$ Hz), 135.3, 133.6 (d, $J = 14.0$ Hz), 129.4 (d, $J = 7.0$ Hz), 122.7, 121.7, 114.7 (d, $J = 15.9$ Hz), 57.6, 55.7; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 72.8. HRMS (EI) calcd for C$_{21}$H$_{17}$Cl$_2$OPS$_4$ [M]$^+$ 513.9277 found: 513.9282.
\[ ^1 \text{H NMR} (400 \text{ MHz, CDCl}_3): \delta 8.21-8.13 (m, 2H), 7.66 (t, J = 1.9 \text{ Hz}, 2H), 7.48 (dq, J = 8.0 \& 1.0 \text{ Hz}, 2H), 7.43-7.40 (m, 2H), 7.26-7.22 (m, 2H), 7.10-7.06 (m, 2H), 6.23 (d, J = 9.1 \text{ Hz}, 2H), 3.88 (s, 3H); ^{13} \text{C} \{ \text{H} \} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 164.4, 139.3 (d, J = 8.0 \text{ Hz}), 133.6 (d, J = 14.0 \text{ Hz}), 132.6, 130.6 (d, J = 35.2 \text{ Hz}), 126.7, 123.1, 122.6, 121.7, 114.7 (d, J = 16.4 \text{ Hz}), 57.5, 55.7. ^{31} \text{P NMR} (162 \text{ MHz, CDCl}_3): \delta 72.6. \text{ HRMS (EI) calcd for C}_{21}H_{17}BrOPS_4 [M]^+: 601.8267 \text{ found: 601.8274. M.P.: 86-90} \text{ °C.} \]

4,6-Bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaposphinane 2-sulfide (1j)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3): \delta 8.19-8.13 (m, 2H), 7.51-7.30 (m, 8H), 7.08-7.05 (m, 2H), 6.23 (d, J = 9.2 \text{ Hz}, 2H), 3.85 (s, 3H); ^{13} \text{C} \{ \text{H} \} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 164.3, 136.6 (d, J = 9.2 \text{ Hz}), 133.7 (d, J = 14.0 \text{ Hz}), 132.3 (d, J = 14.0 \text{ Hz}), 123.5, 122.6, 121.6, 114.7 (d, J = 16.0 \text{ Hz}), 57.7, 55.6; ^{31} \text{P NMR} (162 \text{ MHz, CDCl}_3): \delta 72.6. \text{ HRMS (EI) calcd for C}_{21}H_{17}BrOPS_4 [M]^+: 601.8274 \text{ found: 601.8262.} \]

4,6-Bis(4-iodophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaposphinane 2-sulfide (1k)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3): \delta 8.20-8.13 (m, 2H), 7.73-7.70 (m, 4H), 7.26-7.21 (m, 4H), 7.10-7.01 (m, 2H), 6.20 (d, J = 9.1 \text{ Hz}, 2H), 3.90 (s, 3H); ^{13} \text{C} \{ \text{H} \} \text{NMR} (100 \text{ MHz, CDCl}_3): \delta 164.3, 138.4, 137.1 (d, J = 9.0 \text{ Hz}), 133.8 (d, J = 14.1 \text{ Hz}), 130.9, 129.3, 114.8 (d, J = 16.0 \text{ Hz}), 95.4, 57.7, 55.7; ^{31} \text{P NMR} (162 \text{ MHz, CDCl}_3): \delta 72.7. \text{ HRMS (EI) calcd for C}_{21}H_{17}IOPS_4 [M]^+: 697.7989 \text{ found: 697.7981.} \]
2-(4-Methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1l)

\[
\begin{align*}
&\text{\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.27-8.21 \text{ (m, 2H), 8.02 (d, } J = 1.5 \text{ Hz, 2H), 7.86 (s, 2H), 7.83-7.79 \text{ (m, 6H), 7.60 (dd, } J = 8.5 & 1.9 \text{ Hz, 2H), 7.51-7.46 \text{ (m, 4H), 7.09-7.06 \text{ (m, 2H), 6.52 (d, } J = 9.2 \text{ Hz, 2H), 3.86 (s, 3H); }^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\text{): } \delta 164.2, 135.0, 133.8 \text{ (d, } J = 9.2 \text{ Hz), 133.4 (d, } J = 18.2 \text{ Hz), 129.2, 128.2, 127.8, 126.9, 126.7, 125.4, 123.1, 122.1, 114.7 \text{ (d, } J = 15.9 \text{ Hz), 58.6, 55.8; }^{31}\text{P} \text{ NMR (162 MHz, CDCl}_3\text{): } \delta 72.9.}
\end{align*}
\]

M.P.: 150-155 °C

2-(4-Methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1m)

\[
\begin{align*}
&\text{\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.19-8.13 \text{ (m, 2H), 7.32-7.29 \text{ (m, 2H), 7.25-7.23 \text{ (m, 2H), 7.09-6.97 \text{ (m, 4H), 6.56 (d, } J = 12 \text{ Hz, 2H), 3.88 (s, 3H); }^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\text{): } \delta 164.3, 139.0 \text{ (d, } J = 11.0 \text{ Hz), 138.7, 133.7 \text{ (d, } J = 14.0 \text{ Hz), 127.3 \text{ (d, } J = 12.0 \text{ Hz), 127.1, 126.9, 126.3, 122.4, 121.4, 114.7 \text{ (d, } J = 16.2 \text{ Hz), 55.7, 53.5; }^{31}\text{P} \text{ NMR (162 MHz, CDCl}_3\text{): } \delta 72.5.}
\end{align*}
\]

2-(4-Methoxyphenyl)-4,6-bis(4-nitrophenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1n)

\[
\begin{align*}
&\text{\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.29-8.24 \text{ (m, 5H), 7.72-7.68 \text{ (m, 4H), 7.14-7.10 \text{ (m, 2H), 6.42 (d, } J = 8.0 \text{ Hz, 2H), 3.93 (s, 3H); }^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\text{): } \delta 164.7, 148.3, 143.7 \text{ (d, } J = 8.0 \text{ Hz), 133.7 \text{ (d, } J = 14.0 \text{ Hz), 129.3, 124.7, 124.0, 114.9 \text{ (d, } J = 16.2 \text{ Hz), 57.5, 55.8; }^{31}\text{P} \text{ NMR (162 MHz, CDCl}_3\text{): } \delta 72.9.}
\end{align*}
\]
2. General procedure for table 1

In a sealed tube, 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaporphinane 2-sulfide (1a) (267.9 mg, 0.6 mmol), base (40 mol %) was added in a glove box, followed by diethyl phosphites 2a (55.24 mg, 0.4 mmol) and solvent (2 mL) were added, and stir at 80-100 °C for 8-10 hours. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude product thus obtained was then purified by column chromatography using silica gel (300-400 mesh) (15% ethyl acetate in hexanes) to obtain the pure product of 3a.

Representative example of Table 1: S-Benzyl O,O-diisobutyl phosphorothioate (3a)

Yield: 77.66 mg, 65%; 1H NMR (400 MHz, CDCl3): δ 7.37-7.24 (m, 5H), 4.16-3.96 (m, 6H), 1.28 (t, J=7.2 Hz, 6H); 13C{H}NMR (100 MHz, CDCl3): δ 137.4 (d, J = 6.0 Hz), 128.9, 128.6, 127.6, 63.5 (d, J = 6.0 Hz), 34.9 (d, J = 3.0 Hz), 15.9 (d, J = 7.0 Hz); 31P NMR (162 MHz, CDCl3): δ 27.3.

3. General procedure for Table 2

In a sealed tube, 1 (0.6 mmol), cesium carbonate (40 mol %) in a glove box, then dialkyl phosphites 2 (0.4 mmol) and ethyl acetate (2 mL) were added, the reaction mixture was then heated for 10 hours at 80 °C. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography using silica gel (300-400 mesh) (10-20% ethyl acetate in hexanes) to obtain the pure products 3.

O,O-Diethyl S-(3-methylbenzyl) phosphorothioate (3b)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-m-tolyl-1,3,5,2-trithiaporphinane 2-sulfide (1b) (284.7 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs2CO3 (52.13 mg, 40 mol %) and EA (2.0 mL), then purified by column chromatography (SiO2, ethyl acetate/hexane) to provide 3b.
(66.92 mg, 61% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.27-7.14 (m, 3H), 7.08 (d, \(J = 7.2\) Hz, 1H), 4.18-3.98 (m, 6H), 2.34 (s, 3H), 1.29 (t, \(J = 7.2\) Hz, 6H); \(^{13}\)C{H} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.2, 137.3 (d, \(J = 6.0\) Hz), 129.6, 128.6, 128.4, 125.9, 63.5 (d, \(J = 5.0\) Hz), 34.9 (d, \(J = 4.0\) Hz), 21.3, 15.9 (d, \(J = 8.0\) Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 27.4. HRMS (EI) calcd for C\(_{12}\)H\(_{19}\)O\(_3\)PS [M]\(^+\) 274.0793 found: 274.0784.

**O,O-Diethyl S-(2-methylbenzyl) phosphorothioate (3c)**

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-o-tolyl-1,3,5,2-trithiapinane 2-sulfide (1c) (284.7 mg, 0.6 mmol), diethyl phosphite 2a (55.24 mg, 0.4 mmol), Cs\(_2\)CO\(_3\) (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO\(_2\), ethyl acetate/hexane) to provide 3c as a colorless liquid (65.82 mg, 60% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.31 (d, \(J = 6.8\) Hz, 1H), 7.21-7.13 (m, 3H), 4.18-3.99 (m, 6H), 2.40 (s, 3H), 1.30 (td, \(J = 7.2\) & 0.8 Hz, 6H); \(^{13}\)C{H} NMR (100 MHz, CDCl\(_3\)): \(\delta\) 136.6, 135.1 (d, \(J = 6.0\) Hz), 130.6, 130.0, 128.1, 126.2, 63.5 (d, \(J = 6.0\) Hz), 33.1 (d, \(J = 3.0\) Hz), 19.2, 16.0 (d, \(J = 8.0\) Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 27.4.

**O,O-diethyl S-(4-methylbenzyl) phosphorothioate (3d)**

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-p-tolyl-1,3,5,2-trithiapinane 2-sulfide (1d) (284.7 mg, 0.6 mmol), diethyl phosphite 2a (55.24 mg, 0.4 mmol), Cs\(_2\)CO\(_3\) (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO\(_2\), ethyl acetate/hexane) to provide 3d as a colorless liquid (66.92 mg, 61% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.23 (d, \(J = 8.0\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 4.73-3.98 (m, 6H), 2.32 (s, 3H), 1.29 (t, \(J = 7.2\) Hz, 6H). \(^{13}\)C{H} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.2, 134.2 (d, \(J = 6.0\) Hz), 129.2, 128.7, 63.4 (d, \(J = 5.0\) Hz), 34.6 (d, \(J = 4.0\) Hz), 21.0 (s), 15.8 (d, \(J = 7.0\) Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 27.5. HRMS (EI) calcd for C\(_{12}\)H\(_{19}\)O\(_3\)PS [M]\(^+\) 274.0793 found: 274.0784.
**O,O-diethyl S-(3-methoxybenzyl) phosphorothioate (3e)**

The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaposphinane 2-sulfide (1e) (304.0 mg, 0.6 mmol), diethyl phosphate 2a (55.24 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3e as a colorless liquid (40.66 mg, 35% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 (t, $J = 8.0$ Hz, 1H), 6.95-6.90 (m, 2H), 6.80 (dd, $J = 8.4$ & 2.4 Hz, 1H), 4.17-3.98 (m, 6H), 3.80 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 6H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): $\delta$ 159.6, 138.9 (d, $J = 6.0$ Hz), 129.6, 121.0, 114.3, 113.2, 63.4 (d, $J = 6.0$ Hz), 55.1, 34.8 (d, $J = 4.0$ Hz), 15.8 (d, $J = 8.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 27.3. HRMS (El) calcd for C$_{12}$H$_{19}$O$_4$ PS [M]$^+$ 290.0742 found: 290.0743.

**O,O-diethyl S-(4-methoxybenzyl) phosphorothioate (3f)**

The title compound was prepared following the general procedure for table 2, using 2,4,6-tris(4-methoxyphenyl)-1,3,5,2-trithiaposphinane 2-sulfide (1f) (304.0 mg, 0.6 mmol), diethyl phosphate 2a (55.24 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3f (56.90 mg, 49% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 4.17-3.98 (m, 6H), 3.79 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 6H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): $\delta$ 159.0, 130.1, 129.4 (d, $J = 6.0$ Hz), 114.0, 63.4 (d, $J = 6.0$ Hz), 55.3, 34.5 (d, $J = 4.0$ Hz), 15.9 (d, $J = 8.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 27.5.

**O,O-diethyl S-(4-fluorobenzyl) phosphorothioate (3g)**

The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-
fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1g) (289.4 mg, 0.6 mmol), diethyl phosphite 2a (55.24 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3g (55.65 mg, 50% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.31 (m, 2H), 7.03-6.97 (m, 2H), 4.16-3.97 (m, 6H), 1.29 (td, J = 7.2 & 0.8 Hz, 6H); ¹³C {¹H}NMR (100 MHz, CDCl₃): δ 162.2 (d, J = 236.0 Hz), 133.4 (dd, J = 4.0 & 5.0 Hz), 130.4 (d, J = 9.0 Hz), 115.4 (d, J = 21.0 Hz), 63.5 (d, J = 6.0 Hz), 34.1 (d, J = 3.0 Hz), 15.8 (d, J = 7.0 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 27.1; ¹⁹F NMR (376 MHz, CDCl₃): δ -114.5. HRMS (EI) calcd for C₁₁H₁₆FO₃PS [M]+ 278.0542 found: 278.0544.

S-(4-chlorobenzyl) O,O-diethyl phosphorothioate (3h)³

The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-chlorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1h) (309.2 mg, 0.6 mmol), diethyl phosphite 2a (55.24 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3h (35.28 mg, 30% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.27 (m, 4H), 4.16-3.97 (m, 6H), 1.29 (td, J = 3.2 & 0.8 Hz, 6H); ¹³C {¹H}NMR (100 MHz, CDCl₃): δ 136.2 (d, J = 5.0 Hz), 133.5, 130.3, 128.8, 63.6 (d, J = 5.0 Hz), 34.2 (d, J = 3.9 Hz), 15.9 (d, J = 7.0 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 27.0. HRMS (EI) calcd for C₁₁H₁₆ClO₃PS [M]+ 294.0246 found: 294.0238.

O,O-diethyl S-(3-bromobenzyl) phosphorothioate (3i)

The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1i) (362.6 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3i (56.98 mg, 42% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.52 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 4.17-3.97 (m, 6H), 1.30 (t, J = 0.8 Hz, 6H);
$^{13}$C{H}NMR (100 MHz, CDCl$_3$): δ 139.9 (d, $J = 4.0$ Hz), 131.8, 130.6, 130.1, 127.5, 122.4, 63.6 (d, $J = 6.0$ Hz), 34.2 (d, $J = 4.0$ Hz), 15.9 (d, $J = 7.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.7. HRMS (EI) calcd for C$_{11}$H$_{16}$BrO$_3$PS [M]+ 337.9741 found: 337.9739.

$O,O$-diethyl $S$-(4-bromobenzyl) phosphorothioate (3j)

The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1j) (362.6 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3j (61.05 mg, 45% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.46-7.43 (m, 2H), 7.27-7.22 (m, 2H), 4.16-3.96 (m, 6H), 1.28 (td, $J = 7.2$ & 0.8 Hz, 6H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): δ 136.6 (d, $J = 5.0$ Hz), 131.7, 130.6, 121.5, 63.6 (d, $J = 6.0$ Hz), 34.2 (d, $J = 4.0$ Hz), 15.9 (d, $J = 7.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.9. HRMS (EI) calcd for C$_{11}$H$_{16}$BrO$_3$PS [M]+ 337.9741 found: 337.9739.

$O,O$-diethyl $S$-(4-iodobenzyl) phosphorothioate (3k)

The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-iodophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1k) (419.0 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3k (77.2 mg, 50% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.15-3.94 (m, 6H), 1.28 (td, $J = 7.2$ & 0.8 Hz, 6H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): δ 137.6, 137.2 (d, $J = 5.0$ Hz), 130.7, 93.0, 63.5 (d, $J = 6.0$ Hz), 34.2, 15.8 (d, $J = 8.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 26.8; HRMS (EI) calcd for C$_{11}$H$_{16}$IO$_3$PS [M]+ 385.9602 found: 385.9599.

$O,O$-diethyl $S$-(naphthalen-2-ylmethyl) phosphorothioate (3l)
The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1I) (328.0 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3I (74.48 mg, 60% yield); ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 4.49 (d, J = 12.4 Hz, 2H), 4.16-3.95 (m, 4H), 1.25 (t, J = 7.2 Hz, 6H); ¹³C{H} NMR (100 MHz, CDCl₃): δ 133.6, 132.6 (d, J = 6.0 Hz), 130.89, 128.8, 128.7, 127.6, 126.3, 125.8, 125.2, 123.4, 63.5 (d, J = 6.0 Hz), 32.7 (d, J = 3.0 Hz), 15.8 (d, J = 7.0 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 27.3. HRMS (EI) calcd for C₁₅H₁₅O₃PS [M⁺] 310.0793 found: 310.0789.

**O,O-diethyl S-(thiophen-2-ylmethyl) phosphorothioate (3m)**

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaphosphinane 2-sulfide (1m) (275.1 mg, 0.6 mmol), diethyl phosphite (2a) (55.24 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3m (44.69 mg, 42% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.23 (dd, J = 5.2 & 2.0 Hz, 1H), 7.03 (d, J = 3.2 Hz, 1H), 6.93-6.90 (m, 1H), 4.27 (d, J = 14.0 Hz, 2H), 4.20-4.01 (m, 4H), 1.31(t, J = 7.2 Hz, 6H); ¹³C{H} NMR (100 MHz, CDCl₃): δ 140.0 (d, J = 6.0 Hz), 127.1, 126.9, 125.7, 63.6 (d, J = 5.0 Hz), 29.5 (d, J = 3.0 Hz), 15.9 (d, J = 7.0 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 26.7. HRMS (EI) calcd for C₁₅H₁₅O₃PS₂ [M⁺] 266.0200 found: 266.0206.

**S-benzyl O,O-diisobutyl phosphorothioate (3n)**

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane 2-sulfide (1a) (267.9 mg, 0.6 mmol),
di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3n (88.58 mg, 70% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.24 (m, 5H), 4.04 (d, J = 14.0 Hz, 2H), 3.84-3.78 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.92 (d, J = 1.2 Hz, 6H), 0.90 (d, J = 1.2 Hz, 6H); ¹³C{H} NMR (100 MHz, CDCl₃): δ 137.5 (d, J = 5.0 Hz), 128.9, 128.7, 127.6, 73.3 (d, J = 7.0 Hz), 34.9 (d, J = 3.0 Hz), 28.9 (d, J = 8.0 Hz), 18.7; ³¹P NMR (162 MHz, CDCl₃): δ 27.4.

O,O-Diisobutyl S-(4-methylbenzyl) phosphorothioate (3o)⁵

![Chemical Structure](image)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-p-tolyl-1,3,5,2-trithiaposphinane 2-sulfide (1d) (284.7 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3o (72.69 mg, 55% yield); ¹H-NMR (400 MHz, CDCl₃) δ 7.29-7.26 (m, 2H), 6.86-6.83 (m, 2H), 4.01 (d, J = 13.2 Hz, 2H), 3.84-3.79 (m, 5H), 3.74-3.58 (m, 2H), 1.96-1.85 (m, 2H), 0.93(d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); ¹³C{H} NMR (100 MHz, CDCl₃): δ 159.0, 130.1, 129.4 (d, J = 6.0 Hz), 114.0, 73.3 (d, J = 7.0 Hz), 55.3, 34.4, (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.7. ³¹P NMR (162 MHz, CDCl₃) δ 27.5. HRMS (EI) calcd for C₁₆H₂₇O₃ PS [M]⁺ 330.1419 found: 330.1422.

O,O-Diisobutyl S-(3-methylbenzyl) phosphorothioate (3p)

![Chemical Structure](image)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-m-tolyl-1,3,5,2-trithiaposphinane 2-sulfide (1b) (284.7 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (53.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3p (76.65 mg, 58% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.23 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.91 (t, J = 2.0 Hz, 1H), 6.81 (dd, J = 8.4 & 2.4 Hz, 1H), 4.02 (d, J = 13.6 Hz,
2H), 3.85-3.79 (m, 5H), 3.75-3.69 (m, 2H), 1.96-1.86 (m, 2H), 0.93 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H). $^{13}$C{H} NMR (100 MHz, CDCl$_3$): δ 159.7, 139.0 (d, J = 5.0 Hz), 129.7, 121.2, 114.4, 113.3, 73.4 (d, J = 6.0 Hz), 55.3, 34.9, (d, J = 4.0 Hz), 29.0 (d, J = 7.0 Hz), 18.7. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.4. HRMS (EI) calcd for C$_{16}$H$_2$O$_3$PS [M]$^+$ 330.1419 found: 330.1422.

**O,O-Diisobutyl S-(2-methylbenzyl) phosphorothioate (3q)**

![Structure of 3q](image)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di-o-tolyl-1,3,5,2-trithiaporphinane 2-sulfide (1e) (284.7 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3q (79.30 mg, 60% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32-7.30 (m, 1H), 7.20-7.12 (m, 3H), 4.06 (d, J = 12.0 Hz, 2H), 3.85-3.80 (m, 2H), 3.75-3.70 (m, 2H), 2.40 (s, 3H), 1.97-1.87 (m, 2H), 0.93 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); $^{13}$C{H} NMR (100 MHz, CDCl$_3$): δ 136.6, 135.1 (d, J = 6.0 Hz), 130.5, 129.9, 128.0, 126.2, 73.3 (d, J = 7.0 Hz), 33.0 (d, J = 3.0 Hz), 28.9 (d, J = 7.0 Hz), 19.1, 18.6. $^{31}$P NMR (162 MHz, CDCl$_3$): δ 27.5. HRMS (EI) calcd for C$_{16}$H$_2$O$_3$PS [M]$^+$ 330.1419 found: 330.1416.

**O,O-Diisobutyl S-(3-methoxybenzyl) phosphorothioate (3r)**

![Structure of 3r](image)

The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-methoxyphenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaporphinane 2-sulfide (1e) (304.0 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3r (66.50 mg, 48% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.23 (t, J = 8.0 Hz, 1H), 6.95-6.91 (m, 2H), 6.80 (dd, J = 8.0 & 2.0 Hz, 1H), 4.02 (d, J = 14.0 Hz, 2H), 3.83-3.79 (m, 5H), 3.75-3.71 (m, 2H), 1.96-1.86 (m, 2H), 0.92 (d, J = 1.2 Hz, 6H), 0.91 (d, J = 1.2 Hz, 6H); $^{13}$C{H} NMR (100 MHz, CDCl$_3$) δ 159.7, 138.9 (d, J = 6.0 Hz), 129.7, 121.2, 114.3, 113.2, 73.3 (d, J = 6.0 Hz), 55.2, 34.8 (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.7. $^{31}$P NMR (162 MHz,

**O,O-Diisobutyl S-(4-methoxybenzyl) phosphorothioate (3s)**

The title compound was prepared following the general procedure for table 2, using 2,4,6-tris(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1f) (304.0 mg, 0.6 mmol), diisobutyl phosphate (2b) (77.68 mg, 0.4 mmol), Cs2CO3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO2, ethyl acetate/hexane) to provide 3s (88.67 mg, 64% yield); 1H NMR (400 MHz, CDCl3): δ 7.30-7.26 (m, 2H), 6.87-6.82 (m, 2H), 4.02 (d, J = 13.2 Hz, 2H), 3.84-3.78 (m, 5H), 3.74-3.68 (m, 2H), 1.96-1.87 (m, 3H), 0.93 (d, J = 3.0 Hz, 6H), 0.91 (d, J = 3.0 Hz, 6H); 13C{H} NMR (100 MHz, CDCl3): δ 159.0, 130.1, 129.4 (d, J = 5.0 Hz), 114.4, 73.3 (d, J = 7.0 Hz), 55.3 (s), 34.5 (d, J = 4.0 Hz), 28.9 (d, J = 8.0 Hz), 18.6; 31P NMR (162 MHz, CDCl3): δ 27.6. HRMS (EI) calcd for C16H27O4PS [M]+ 346.1368 found: 346.1363.

**S-(4-Fluorobenzyl) O,O-diisobutyl phosphorothioate (3t)**

The title compound was prepared following the general procedure for table 2 using 4,6-bis(4-fluorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1g) (289.4 mg, 0.6 mmol), di-isobutyl phosphate (2b) (77.68 mg, 0.4 mmol), Cs2CO3 (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO2, ethyl acetate/hexane) to provide 3t (77.57 mg, 58% yield); 1H NMR (400 MHz, CDCl3): δ 7.36-7.32 (m, 2H), 7.03-6.98 (m, 2H), 4.03 (d, J = 14.0 Hz, 2H), 3.84-3.78 (m, 2H), 3.74-3.68 (m, 2H), 1.95-1.87 (m, 2H), 0.92 (d, J = 6.8 Hz, 12H); 13C{H} NMR (100 MHz, CDCl3): δ 161.6 (d, J = 170.0 Hz), 133.2 (d, J = 125.0 Hz), 130.4 (d, J = 9.0 Hz), 115.6 (d, J = 21.0 Hz), 73.4 (d, J = 7.0 Hz), 34.2 (d, J = 4.0 Hz), 29.0 (d, J = 7.0 Hz), 18.7; 31P NMR (162 MHz, CDCl3): δ 27.1; 19F NMR (376 MHz, CDCl3): δ -114.5. HRMS (EI) calcd for C15H24FO3PS [M]+ 334.1168 found: 334.1172.

**S-(4-Chlorobenzyl) O,O-diisobutyl phosphorothioate (3u)**
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-chlorophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1h) (309.2 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3u (70.16 mg, 50% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.27 (m, 4H), 4.01 (d, J = 14.4 Hz, 2H), 3.83-3.77 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.91 (d, J = 6.8 Hz, 12H); ¹³C [H] NMR (100 MHz, CDCl₃): δ 136.2 (d, J = 5.0 Hz), 133.4, 130.3, 128.8, 73.4 (d, J = 7.0 Hz), 34.2 (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.6. ³¹P NMR (162 MHz, CDCl₃): δ 27.0. HRMS (EI) calcd for C₁₅H₂₄ClO₃PS [M]⁺ 350.0872 found: 350.0869.

S-(3-Bromobenzyl) O,O-diisobutyl phosphorothioate (3v)

The title compound was prepared following the general procedure for table 2, using 4,6-bis(3-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1i) (362.6 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3v (102.77 mg, 65% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.52 (t, J = 1.6 Hz, 1H), 7.40-7.37 (m, 1H), 7.31-7.27 (m, 1H), 7.19 (t, J = 8.0 Hz, 1H), 3.98 (d, J = 14.8 Hz, 2H), 3.84-3.79 (m, 2H), 3.74-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.92 (d, J = 0.8 Hz, 6H), 0.90 (d, J = 1.2 Hz, 6H); ¹³C [H] NMR (100 MHz, CDCl₃): δ 134.0 (d, J = 5.0 Hz), 125.8, 124.6, 124.1, 121.5, 116.4, 67.3 (d, J = 7.0 Hz), 28.1, 22.8 (d, J = 8.0 Hz), 12.6; ³¹P NMR (162 MHz, CDCl₃): δ 26.85. HRMS (EI) calcd for C₁₅H₂₃BrO₃PS [M]⁺ 394.0367 found: 394.0358.

S-(4-bromobenzyl) O,O-diisobutyl phosphorothioate (3w)
The title compound was prepared following the general procedure for table 2, using 4,6-bis(4-bromophenyl)-2-(4-methoxyphenyl)-1,3,5,2-trithiaphosphinane 2-sulfide (1j) (362.6 mg, 0.6 mmol), di-isobutyl phosphate (2b) (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3w (109.10 mg, 69% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.46-7.43 (m, 2H), 7.26-7.23 (m, 2H), 3.99 (d, J = 14.8 Hz, 2H), 3.85-3.77 (m, 2H), 3.73-3.67 (m, 2H), 1.95-1.85 (m, 2H), 0.91 (d, J = 6.8 Hz, 12H). ¹³C{H} NMR (100 MHz, CDCl₃): δ 136.7 (d, J = 5.0 Hz), 131.7, 130.6, 121.5, 73.4 (d, J = 6.0 Hz), 34.2 (d, J = 4.0 Hz), 28.8 (d, J = 8.0 Hz), 18.6. ³¹P NMR (162 MHz, CDCl₃): δ 26.9. HRMS (EI) calcd for C₁₅H₂₄BrO₃PS [M]+= 394.0367 found: 394.0364.

**S-(4-Iodobenzyl) O,O-diisobutyl phosphorothioate (3x)**

![Diagram of S-(4-Iodobenzyl) O,O-diisobutyl phosphorothioate (3x)](image)

The title compound was prepared following the general procedure for table 2, using 4-iodobenzaldehyde 1k (148.8 mg, 0.6 mmol), di-isobutyl phosphate 2b (419.0 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3x (72.53 mg, 41% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.64 (dt, J = 8.8 & 2.4 Hz, 2H), 7.12 (dt, J = 8.8 & 2.4 Hz, 2H), 3.98 (d, J = 14.8 Hz, 2H), 3.82-3.77 (m, 2H), 3.72-3.66 (m, 2H), 1.94-1.84 (m, 2H), 0.91 (d, J = 0.8 Hz, 6H), 0.90 (d, J = 0.8 Hz, 6H); ¹³C{H} NMR (100 MHz, CDCl₃): δ 137.7, 137.5 (d, J = 5.0 Hz), 130.9, 93.0, 73.4 (d, J = 7.0 Hz), 34.4 (d, J = 4.0 Hz), 28.9 (d, J = 8.0 Hz), 18.7; ³¹P NMR (162 MHz, CDCl₃): δ 26.9. HRMS (EI) calcd for C₁₅H₂₄BrO₃PS [M]+= 442.0228 found: 442.0234.

**O,O-Diisobutyl S-(4-nitrobenzyl) phosphorothioate (3y)**

![Diagram of O,O-Diisobutyl S-(4-nitrobenzyl) phosphorothioate (3y)](image)

The title compound was prepared following the general procedure for table 2, using 4-nitrobenzaldehyde 1n (100.3 mg, 0.6 mmol), di-isobutyl phosphate 2b (77.68 mg, 0.4 mmol), Cs₂CO₃ (52.13 mg, 40 mol%) and EA (2.0 mL), then purified by column chromatography (SiO₂, ethyl acetate/hexane) to provide 3y (43.36 mg, 30% yield); ¹H NMR (400 MHz, CDCl₃): δ 8.20-8.16 (m, 2H), 7.58-7.55 (m, 2H), 4.12 (d, J = 15.6 Hz, 2H), 3.84-
3.75 (m, 2H), 3.74-3.68 (m, 2H), 1.95-1.85 (m, 2H), 0.85 (d, J = 6.9 Hz, 12H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): δ 147.2, 145.4 (d, J = 4.0 Hz), 129.7, 123.8, 73.6 (d, J = 7.0 Hz), 34.0 (d, J = 4.0 Hz), 29.8 (d, J = 7.0 Hz), 18.6; $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.2. HRMS (El) calcd for C$_{15}$H$_{24}$NO$_3$PS $[M]^+ 366.1113$ found: 366.1117.

**O,O-diisobutyl S-(naphthalen-2-ylmethyl) phosphorothioate (3z)**

![Diagram](image1)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(naphthalen-2-yl)-1,3,5,2-trithiaposphinane 2-sulfide (1l) (328.0 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%), and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3z (89.41 mg, 61% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.39-7.35 (m, 1H), 4.51 (d, J = 12.4 Hz, 2H), 3.83-3.76 (m, 2H), 3.73-3.67 (m, 2H), 1.92-1.82 (m, 2H), 0.89 (d, J = 4.0 Hz, 6H), 0.87 (d, J = 4.0 Hz, 6H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$) δ 133.7, 132.6 (d, J = 6.0 Hz), 130.9, 128.77, 128.70, 127.6, 126.3, 125.8, 125.2, 123.5, 73.2 (d, J = 7.0 Hz), 32.6 (d, J = 4.0 Hz), 28.7 (d, J = 7.0 Hz), 18.5; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.4. HRMS (El) calcd for C$_{19}$H$_{27}$O$_3$PS $[M]^+ 366.1419$ found: 366.1416.

**O,O-diisobutyl S-(thiophen-2-ylmethyl) phosphorothioate (3aa)**

![Diagram](image2)

The title compound was prepared following the general procedure for table 2, using 2-(4-methoxyphenyl)-4,6-di(thiophen-2-yl)-1,3,5,2-trithiaposphinane 2-sulfide (1m) (275.1 mg, 0.6 mmol), di-isobutyl phosphite (2b) (77.68 mg, 0.4 mmol), Cs$_2$CO$_3$ (52.13 mg, 40 mol%), and EA (2.0 mL), then purified by column chromatography (SiO$_2$, ethyl acetate/hexane) to provide 3aa (54.16 mg, 42% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.22 (dd, J = 5.2 & 1.2 Hz, 1H), 7.03 (dd, J = 3.6 & 1.2 Hz, 1H), 6.91 (dd, J = 5.2 & 3.6 Hz, 1H), 4.28 (d, J = 13.6 Hz, 2H), 3.88-3.82 (m, 2H), 3.78-3.72 (m, 2H), 1.99-1.88 (m, 2H), 0.93 (d, J = 17.0 Hz, 12H); $^{13}$C{H}NMR (100 MHz, CDCl$_3$): δ 140.0 (d, J = 6.0 Hz), 127.1, 126.8, 125.6, 73.3 (d, J = 7.0 Hz), 73.0 (d, J = 17.0 Hz), 71.2 (d, J = 17.0 Hz), 70.3 (d, J = 17.0 Hz), 38.0 (d, J = 17.0 Hz).
Hz), 29.4 (d, J = 3.0 Hz), 28.9 (d, J = 8.0 Hz), 18.6; $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 26.7. HRMS (EI) calcd for C$_{13}$H$_{23}$O$_3$PS$_2$ [M]$^+$ 322.0826 found: 322.0819.

4. References
(1H NMR, CDCl₃, 400 MHz)

(13C{¹H} NMR, CDCl₃, 100 MHz)
(¹³C{¹H} NMR, CDCl₃, 100 MHz)

![NMR Spectrum](image1)

(¹³P NMR, CDCl₃, 162 MHz)

![NMR Spectrum](image2)
(1H NMR, CDCl₃, 400 MHz)

(13C NMR, CDCl₃, 100 MHz)
$^1$H, $^{13}$C, $^{31}$P & $^{19}$F NMR spectra of compounds 3
**Issue in honor of Professor Tien-Yau Luh**

**ARKIVOC 2023, ii, S1-S84**

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**$^{13}$C NMR, CDCl$_3$, 100 MHz**

![NMR spectrum of $^{13}$C]  

**$^{31}$P NMR, CDCl$_3$, 162 MHz**

![NMR spectrum of $^{31}$P]
(19F NMR, CDCl₃, 376 MHz)

(19P NMR, CDCl₃, 162 MHz)
(\textsuperscript{1}^3 \text{C}[\text{H}] \text{NMR, CDCl}_3, 100 \text{ MHz})

3k

(\textsuperscript{31} \text{P NMR, CDCl}_3, 162 \text{ MHz})

3k
\textsuperscript{(1}H NMR, CDCl\textsubscript{3}, 400 MHz)
$^{13}$C NMR, CDCl$_3$, 100 MHz

$^{31}$P NMR, CDCl$_3$, 162 MHz
(\textsuperscript{1}H NMR, CDCl\textsubscript{3}, 400 MHz)

(\textsuperscript{13}C NMR, CDCl\textsubscript{3}, 100 MHz)
\(^{31}\)P NMR, CDCl\(_3\), 162 MHz

\(^{1}H\) NMR, CDCl\(_3\), 400 MHz
(31P NMR, CDCl₃, 162 MHz)

3t

(19F NMR, CDCl₃, 376 MHz)

3t
(1H NMR, CDCl₃, 400 MHz)

(13C [H] NMR, CDCl₃, 100 MHz)
(^1H NMR, CDCl₃, 400 MHz)

(13 C{[H]} NMR, CDCl₃, 100 MHz)